RB-36

LUMINESCENCE IN ELECTRONICALLY ACTIVE SOLIDS

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This bulletin describes the three basic electronic activities in phosphors and other electronically active solids. These activities are: (1) orientation of spin, (2) excitation leading to radiation, and (3) unilateral displacement. Atomic interaction provides, through chemical synthesis, effective means for modifying, controlling, and combining these electronic activities. Research in this field has made many physical phenomena tractable and useful, and has afforded greater understanding of the fundamental natures of solids and of luminescence.

Electrons are the lightest of all the known stable, charged, elementary particles, despite the many elementary particles that have been discovered during studies of cosmic rays and atomic nuclei. A few decades ago, considerable research effort was concentrated on producing and controlling free electrons *in vacuo*, where the problems are chiefly those of classical physics. More recently, research effort has been concentrated on modifying and controlling the behaviors (activities) of bound and quasi-free electrons in solids, where the problems are chiefly those of quantum physics.

The most potent means for modifying the activities of electrons in solids is by short-range interaction of atoms. Atomic interactions are brought about by chemical reactions, and so efficient solid-state research uses both chemistry and physics to synthesize and study solids.[1] Fundamentally, one seeks to alter electronic activity by varying the neighbors of an atom, or discrete group of atoms, to which the active (outer, loosely bound) electron is attached. This procedure is very familiar in phosphor research, wherein impurities, such as activator or trapping atoms, are incorporated in different host crystals to achieve different electronic behaviors. Phosphors are in many respects representative of the general class of electronically active solids.

Phosphors exhibit, or are affected by, all three of the important electronic activities in solids. These basic electronic activities are:

1. Electron-spin *orientation.*
2. Electron *excitation→radiation.*
3. Electron *displacement.*

The natures and magnitudes of the basic electronic activities in solids are next outlined, in the order given, with indications of the relations between these activities and luminescence.

The *spin-orientation* activity, when it occurs as a cooperative interaction and alignment of unpaired spins in near-neighbor atoms, produces *ferromagnetism* and *antiferromagnetism*, corresponding to parallel and antiparallel spin-vector orientations. For a strong ferromagnetic solid, such as crystalline iron, with 10^{23} atoms per cubic centimeter and two unpaired spins per atom, the total magnetic spin moment would be, using the value of 5.8×10^{-9} ev oersted^{-1} for the Bohr magneton,

$$I_s = 10^{23} \, cm^{-3} \times 2 \times 5.8 \times 10^{-9} \, ev \, oersted^{-1} \qquad (1)$$

$$\approx 10^{15} \, ev \, oersted^{-1} \, cm^{-3} \qquad (2)$$

Strong ferromagnetism, which was formerly provided chiefly by conducting metals and alloys, is now provided by semiconducting and nearly insulating ferromagnetic spinels.[2]

Electron-spin interactions and orientations are important in phosphors, such as *rhbdl.-Zn_2SiO_4:Mn*, that have transition-element activators with unpaired electron spins. In such phosphors, there are two antithetic electron-spin activities. First, luminescence is *enabled* by subatomic electron-spin regroupings[3] that provide inner, shielded, excited states where high-energy excitation quanta can be localized, and from which radiative transitions occur to the ground state. Here, the input excitation energy works against the basic electrostatic-repulsion energy that drives the inner, incompleted-shell electrons of the activator atom into a ground-state condition of maximum spin unpairing corresponding to minimum energy (Hund's rule). Another luminescence-enabling effect involves spin-orbit coupling through covalent bonding, to be discussed later in this bulletin. Second, luminescence is *suppressed* by certain interatomic electron-spin interactions that (1) decrease the number of unpaired electron spins and regrouping states available for radiative tran-

sitions, and (2) decrease radiative transitions by permitting transfer of energy from an excited activator atom to an unexcited atom.[4] Such energy transfer de-localizes the excitation, and increases the probability of dissipating high-energy excitation quanta by conversion into low-energy phonons. Hence, the interacting atoms in a ferromagnetic or antiferromagnetic solid do not function well as luminescence centers. Conversely, efficient phosphors are diamagnetic or paramagnetic.

The *electron-excitation and radiation* activity in stable solids includes (1) absorption and appreciable temporary localization of high-energy quanta in excited states from which radiative transitions produce *luminescence*, as in phosphors, and (2) absorption of primary energy with practically complete degradation-plus-diffusion into low-energy phonons to produce *thermal radiation*, as in pigments and incandescent solids. Excitation in *incandescence* involves the indirect step of agitating atomic nuclei which are, on the average, about 200,000 times more ponderous than electrons. Excitation in *luminescence*, on the other hand, involves relatively direct energizing of the active electron. Direct energizing affords the efficient and instantaneous production of luminescence radiation that has made possible fluorescent lamps, television, radar, electron microscopes, scintillation counters, and other modern developments.

For an efficient luminescent solid, such as *rhbdl.-Zn_2SiO_4:Mn,* with one activator atom (Mn) per 350 host-crystal atoms, i.e., *2.4 x 10^{20} Mn* atoms (ions) per cubic centimeter, the maximum observed luminescence radiation output, L, per unit of excited volume, under high-intensity excitation, is[5]

$$L_{sustained\ excitation} \approx 10^{20}\ photons\ cm^{-3}\ sec^{-1} \quad (3)$$

$$\approx 2 \times 10^{20}\ ev\ cm^{-3}\ sec^{-1} \quad (4)$$

$$L_{pulsed\ excitation} \approx 4 \times 10^{22}\ photons\ cm^{-3}\ sec^{-1} \quad (5)$$

$$\approx 8 \times 10^{22}\ ev\ cm^{-3}\ sec^{-1} \quad (6)$$

Comparison of the *4 x 10^{22}* photons cm^{-3} sec^{-1} with the *2.4 x 10^{20}* Mn-atoms cm^{-3} shows that each *Mn* atom is excited and emits, on the average, every 0.006 second. This time is substantially the same as the measured characteristic decay time of about 0.01 second.

For a phosphor of efficiency $\mathcal{E}$ under sustained excitation, at saturation intensity, the maximum luminescence output, L_m, of photons with energy $h\nu$, is related to the number of emissive centers per excited unit volume, δ, and the average lifetime, $\bar{\tau}$, by[21]

$$L_{m(sustained\ excit.)} = \mathcal{E}h\nu\delta\bar{\tau}^{-1}\ ev\ cm^{-2}\ sec^{-1} \quad (7)$$

Under pulsed excitation, when the interval between pulses is much longer than $\bar{\tau}$, the determining factor is δ; i.e.,[21]

$$L_{m(pulsed\ excit.)} \propto \delta \quad (8)$$

The time aspect of luminescence is of fundamental significance. For an allowed radiative transition of an isolated atom, the natural excited-state lifetime, τ_f, is related to the transition probability per unit time, P, and the natural half-width of the emission line, $\Delta\nu$, by[6]

$$\tau_f = P^{-1} = 2\pi(\Delta\nu)^{-1}\ sec^{-1} \quad (9)$$

where, classically, for emitted photons of frequency, ν_o, and corresponding wavelength λ_o (in cm)

$$\Delta\nu = 1.17 \times 10^{-12} c^{-1} \nu_o^2\ sec^{-1} \quad (10)$$

$$= 1.17 \times 10^{-12} c\lambda_o^{-2}\ sec^{-1} \quad (11)$$

from which the energy width of the emission line is

$$\Delta E = h(\Delta\nu) \quad (12)$$

$$= 1.65 \times 10^{-37} \nu_o^2\ ev \quad (13)$$

$$= 1.45 \times 10^{-16} \lambda_o^{-2}\ ev \quad (14)$$

and, according to the indeterminacy principle, the minimum value of τ_f is

$$\tau_{f(min.)} \approx h/2\pi\Delta E \quad (15)$$

From Eqs. (14) and (15) one obtains for optical photons with 6000-Å wavelength, $\Delta E \approx 4 \times 10^{-8}$ ev, and $\tau_{f(min.)} \approx 1.6 \times 10^{-8}$ second.

The purely radiative (temperature-independent) component of the decay times of known efficient phosphors has values that range from about 10^{-8} second to over 10^{-1} second.[7] Effective decay-time values, τ_e, somewhat less than 10^{-8} second can be obtained, with sacrifice in efficiency, by introducing competitive non-radiative processes, such as by: (1) increasing activator proportions beyond the optimum for maximum efficiency, or (2) increasing the operating temperature of the phosphor beyond the temperature breakpoint.[8] Both of these methods of decreasing τ_e utilize the well-known relation for phosphors[9]

$$L = L_o \epsilon^{-(a+\nu_a\epsilon^{-E^*/kT})t} \quad (16)$$

and

$$\tau_e = (a+\nu_a\epsilon^{-E^*/kT})^{-1} \quad (17)$$

The exponential (non-radiative) term in Eq. (17) may be increased by either decreasing E^* (e.g., by unduly increasing the proportion of activator), or by increasing the temperature, T.

Decay-time values greater than 10^{-8} second can be obtained by (1) using partially allowed transitions in

isolated atoms, and (2) altering the transition probabilities of excited atoms, *e.g.*, by subjecting them to the force fields of neighboring atoms in solids. Both of these methods of modifying τ are exemplified by the different decay times of $Mn(2+)$ incorporated in different host crystals, as shown in Table I.

TABLE I

Excited-state lifetimes, τ, of some phosphors with about 0.3% (by weight) of manganese activator.[10]

Host Crystal	Activator*	τ (sec)
ZnF_2	Mn(2+)	0.1
$CdSO_4$	"	0.05
$MgSO_4$	"	0.03
$Zn_3(PO_4)_2$	"	0.02
$CdSiO_3$	"	0.019
$Zn_2B_2O_5$	"	0.018
$Cd_2B_2O_5$	"	0.015
Zn_2SiO_4	"	0.013
Zn_2GeO_4	"	0.0105
$ZnAl_2O_4$	"	0.0055
$ZnGa_2O_4$	"	0.0043
ZnS	"	~ 0.0004**

* The parentheses (2+) indicate that there is some covalent character to the bonding.

** The decay-time for ZnS:Mn is not for a pure radiative decay, because the measured value decreases with increasing intensity of primary-electron excitation.[10] (According to Dr. R. H. Bube, however, the value for the pure radiative decay is approximately the value given.)

There is now good evidence[11] for identifying the emission transition of $Mn(2+)$ in the listed solids as $4G \longrightarrow 6S$, which involves the following electron-spin regrouping in the inner, incomplete 3d shell of $Mn(2+)$:

(18)

$$Excited\,state,\ 3d^5, \uparrow\uparrow\uparrow\uparrow\downarrow \longrightarrow Ground\,state,\ 3d^5, \uparrow\uparrow\uparrow\uparrow\uparrow$$

The $4G \longrightarrow 6S$ transition is forbidden on a spin-only basis, and it has been deduced by D. S. McClure that appreciable spin-orbit coupling probably occasions the observed emission, most likely by mixing some $4P$ character into the $6S$ ground state.[12] The transition probability for the isolated ion would then be

$$P = \tau^{-1} = 10^8\ (\Lambda/\Delta\bar{\nu})^2\ sec^{-1} \qquad (19)$$

where Λ is the coefficient of spin-orbit coupling (about 80 for $4P/6S$), and $\Delta\bar{\nu}$ is the wave-number separation between the mixed states (26,800 cm^{-1} for $4P - 6S$). For an

isolated ion of Mn^{2+}, then, τ is calculated to be 0.001 second. In a solid, the value of $\Delta\nu$ for $4P - 6S$ increases (whereas that for $4G - 6S$ decreases, and τ also increases).

The nature and strength of interatomic bonding in the host crystal strongly influence the value of τ. For this purpose, and for the purpose of influencing many other electronic activities, inorganic solids are more versatile than organic solids, because inorganic solids permit (1) greater use of ionic, covalent, and intermediate types of bonding, (2) use of combinations of all of the known species of atoms, without restriction to compounds of carbon, and (3) use of greater bonding energies, as attested by the high melting points of inorganic solids. To obtain larger values of τ, starting with an emissive atom in a given solid, one may use instead other host-crystal solids with (1) less bonding energy, (2) less covalent bonding, and (3) lighter atoms as near-neighbors to the emissive atom. Correspondingly, smaller values of τ are obtainable by using higher bonding energy, and more covalent bonding to heavier neighboring atoms (or by using the means described in connection with Eq. (16)). When there is considerable covalent bonding, electrons of the emissive atom spend part of their time in the neighboring atoms where increased spin-orbit coupling may be occasioned during transits in the more intense fields of heavier neighboring nuclei.

The growth (rise) of luminescence for phosphors with simple exponential decays, as in Eq. (16), proceeds according to

$$L = \sigma N_o \tau_e^{-1}[1 - \epsilon^{-(\sigma + \tau_e^{-1})\,t}]\,/\,(\sigma + \tau_e^{-1}) \qquad (20)$$

where σ is proportional to the excitation density, and N_o is the number of emissive centers per unit volume.[13] According to Eq. (20), the time required to attain equilibrium radiation output, L, is proportional to τ_e for values of σ below saturation, and may be decreased by increasing σ above the value needed for saturation (where saturation means that all of the N_o centers are in continuous operation).

The previous examples of ability to vary the time factor in luminescence is indicative of the progress that has been made in modifying and controlling electronic behavior in solids. Other prominent examples in the phosphor field are (1) extension of the time scale by introducing trapping,[14] and (2) altering the dominant wavelengths (emission colors) of phosphors.[15]

The *electron-displacement* activity in solids uses chiefly the ability of electrons as carriers of charge and energy to produce electrical phenomena, such as *ferroelectricity, pyroelectricity, piezoelectricity, conduction, semiconduction, photoconduction, thermionic emission, photoemission,* and *secondary emission.* The dielectric phenomena involve unilateral displacements of bound electrons

(or nuclei) localized in solids, the conduction phenomena involve quasi-free electrons moving through solids, and the emission phenomena provide free electrons *in vacuo*.

The magnitudes of electron-displacement activities in and on solids can be very large. For example, even a normally insulating solid, such as barium oxide, can provide as much as 100 amperes per square centimeter during pulsed thermionic emission.[16] The electron-flow density, I_e, is then

$$I_e = 6 \times 10^{20} \; electrons \; cm^{-2} \; sec^{-1} \qquad (21)$$

If the electrons have, on the average, kT energy, then the energy-flow density, I_{ev}, at 1200 degrees K, is

$$I_{ev} \approx 6 \times 10^{19} \; ev \; cm^{-2} \; sec^{-1} \qquad (22)$$

In phosphors, it is necessary to localize relatively high-energy quanta ($\approx 3 \; ev$) to minimize dissipation of energy during the lifetimes of the excited electrons.[17] Energy localization is best done in solids wherein more than $30kT$ energy is required to free bound electrons. In phosphors intended for operation at room-temperature, therefore, the width of the forbidden band of the host crystal should exceed one electron volt, and preferably exceed three electron volts for efficient production of visible radiation. Hence, the most suitable phosphor host crystals are insulators or poor semiconductors.

Electron displacement may be, *but need not be*, part of the luminescence mechanism. The basic luminescence process is simply a localized excitation (*e.g.*, by direct absorption of a primary ultraviolet photon by an atom) followed by a localized radiative transition (*e.g.*, producing an optical photon), without any unilateral displacement of electrons relative to a positively charged atomic nucleus. It is possible and useful, however, to have electron displacements during (1) primary processes preceding localized excitation, and (2) secondary processes between the primary absorption of energy and the final localized excitation giving luminescence emission. Cathodoluminescence, roentgenoluminescence, and "electroluminescence" have electron displacements during the primary process leading to excitation, and cathodoluminescence requires secondary emission to prevent charging of the phosphor particles.[18] Phosphors with non-exponential decays have electron displacements and trapping during the secondary process.

Auxiliary electron displacements provide more degrees of freedom in luminescence of solids, and expand the ranges of certain properties of phosphors. The range of kinetic energies of primary electrons capable of producing cathodoluminescence extends from nearly zero[19] to many millions of electron volts. Also, the secondary process of electron displacement and trapping provides means for controllably increasing the time between primary energy input and luminescence radiation output from about 10^{-8} second to many years. Another impressive combination of the basic electron-displacement and electron-excitation ($\longrightarrow$ radiation) activities is found in "electroluminescence", such as the alternating-field "electroluminescence" of G. Destriau.[20] The potentialities of (1) the innumerable possible combinations of atoms to provide different electronic behaviors in solids, and (2) the variety of combinations and interactions of the different electron activities offer ample incentive for continued research on phosphors and other electronically active solids.

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